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# The catalytic reduction of NO by H<sub>2</sub> on Ru(0001): Observation of NH<sub>ads</sub> species

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## Abstract

Adsorption of NO and the reaction between NO and H<sub>2</sub> were investigated on the Ru(0001) surface by X-ray photoelectron spectroscopy (XPS). Surface composition was measured after NO adsorption and after the selective catalytic reduction of nitric oxide with hydrogen in steady-state conditions at 320 K and 390 K in a 30:1 mixture of H<sub>2</sub> and NO (total pressure = 10<sup>−4</sup> mbar). After steady-state NO reduction, molecularly adsorbed NO in both the linear on-top and threefold coordinations, NH<sub>ads</sub> and N<sub>ads</sub> species were identified by XPS. The coverage of the NH<sub>ads</sub> and N<sub>ads</sub> species was higher after the reaction at 390 K than the corresponding values at 320 K. Strong destabilisation of N<sub>ads</sub> by O<sub>ads</sub> was detected. A possible reaction mechanism is discussed.

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## 1. Introduction

Among the group VIII transition metals ruthenium is an object of particular interest because of its well-known catalytic activity towards several processes. In the synthesis of ammonia, it has found an industrial application in the Kellogg Advanced Ammonia Process (KAAP) [1,2], the selective catalytic reduction of nitrogen oxides [3,4], Fischer–Tropsch synthesis [5] and the hydrogenolysis of hydrocarbons [6]. The practical difficulties in the utilisation of Ru-based catalysts for the catalytic reduction of NO are connected with the formation of noxious volatile ruthenium oxides at high temperatures in the presence of gas phase oxygen. However, the remarkable selectivity of

ruthenium in NO reduction with hydrogen or ammonia to N<sub>2</sub> makes it an attractive object of study.

NO on the Ru(0001) surface has been subject of a number of theoretical and experimental studies [7–23], whereas less attention has been devoted to the reaction between H<sub>2</sub> and NO on ruthenium single crystals [11,24,25]. According to high-resolution energy electron loss spectroscopy (HREELS) and IR absorption spectroscopy (IRAS), below 200 K NO adsorbs molecularly either in threefold hollow and/or on-top positions [7,8,13,18]. Two NO stretching vibrations at approximately 1500 cm<sup>−1</sup>,  $\nu_1$ , and 1800 cm<sup>−1</sup>,  $\nu_2$ , were assigned to the threefold and on-top coordinated species, respectively. A detailed LEED-IV analysis [19,22] and a combined theoretical and experimental study by X-ray emission spectroscopy (XES) [21,23] showed the existence of three adsorption sites in the saturated NO<sub>ads</sub> layer on Ru(0001). NO was found to adsorb on NO<sub>top</sub>, NO<sub>hcp</sub> and NO<sub>fcc</sub> sites in upright orientations with the nitrogen end down. An N–O bond length for

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the NO<sub>top</sub> state is shorter than those for the bridge coordination [14,19,22]. The change of the N–O bond length agrees with the classic Blyholder model [26], according to which bonding of a NO molecule to a transition metal can be divided into  $\sigma$  donation and  $\pi$  back donation. As roughly estimated by a Mulliken population analysis [21], the adsorption complex in the hollow site experiences a substantially stronger back donation in comparison to the on-top site. The charge transfer at the hexagonal-close-packed (hcp) site is slightly higher than at the face-centred-cubic (fcc) site. Detailed discussion of the  $\pi$  back donation questions can be found elsewhere [21].

At room temperature and low coverage, NO dissociates completely on the Ru(0001) surface [9,17,20]. The dissociation takes place on the active sites with low coordination such as an atomic step [17]. The molecular adsorption states of NO,  $\nu_1$  and  $\nu_2$ , are formed at high coverage [9].

Ru/MgO was found to be a highly active catalyst for the reduction of NO by H<sub>2</sub> to N<sub>2</sub> [3,27]. On the other hand, ruthenium is a good catalyst for the ammonia production. The question is, how does ruthenium behave so differently in these reactions? In order to answer this question, the basic knowledge of the composition of the adsorption layers and of the surface processes such as reaction, adsorption, surface diffusion, etc. is necessary. As discussed in Ref. [3] the thermal desorption data from the Ru/MgO catalysis exhibited remarkable similarity to corresponding results obtained with the Ru(0001) single crystal under UHV. Therefore, the Ru(0001) single crystal may well serve as an adequate model system for Ru supported catalysts. The present paper focuses on the ex situ XPS study of the steady-state NO + H<sub>2</sub> reaction on the Ru(0001) surface at total pressure 10<sup>−4</sup> Torr. The “low-pressure/single-crystal” results were compared with the finding for the Ru/MgO catalyst [3,27]. Since, the literature results deal mainly with low-temperature NO, adsorption of NO at 300 K on the Ru(0001) surface was studied as well. Also, XPS has several advantages compared to EELS and IRAS/RAIRS, which were employed before, because XPS provides quantitative and qualitative information on the surface composition and all adsorbed species (NO, N, NH<sub>x</sub>, O) can be detected simultaneously.

## 2. Experimental

The experiments were carried out in the stainless steel chamber of the modified Leybold LHS 12 MCD system equipped with facilities for ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) (base pressure  $\leq 10^{-10}$  mbar). The XPS data were obtained using the MgK $\alpha$  radiation ( $h\nu = 1253.6$  eV) and a fixed analyzer pass energy of 48 eV, corresponding to a resolution of 0.95 eV, which was measured as a full width at half maximum (FWHM) of the Ru3d<sub>5/2</sub> peak. Binding energy (BE) was referred to the Fermi level and the linearity and slope were calibrated using the Au4f<sub>7/2</sub> = 84.0 eV and Cu2p<sub>3/2</sub> =

932.7 eV peaks. The Ru3d<sub>5/2</sub> peak was set at a BE of 280.1 eV.

A Ru single crystal used in the experiments was oriented along the (0001) direction within  $<0.5^\circ$ . The single crystal was spot-welded between two tungsten wires and was heated resistively. The temperature of the single crystal was measured by means of a chromel–alumel thermocouple spot-welded to an edge of the crystal. The cleaning procedures included Ar<sup>+</sup>-etching followed by annealing cycles in oxygen and in vacuum, and flashing up to 1500 K in vacuum. The cleanliness of the sample was checked by XPS and UPS prior to each experiment.

Reaction and gas exposure were performed in the stainless steel preparation chamber (base pressure  $\leq 1 \times 10^{-9}$  mbar). The sample was then transferred to the UHV analyzer chamber within  $\approx 1$  min. Gas exposures were measured in Langmuir (L), 1 L being 10<sup>−6</sup> Torr s. Nitric oxide with a purity of 99.95% and high-purity (99.9999%) hydrogen, both supplied by Linde, were used for the experiments without further purification.

The coverage was measured in monolayer (ML) in respect of the number of ruthenium atoms in the topmost layer which for Ru(0001) equals to  $1.58 \times 10^{15}$  atoms cm<sup>−2</sup> [9]. The concentrations of the chemical elements in the near-surface region were estimated after the subtraction of a Shirley type background, taking into account the corresponding atomic sensitivity factors [28]. The surface concentrations of the oxygen-containing species (NO<sub>ads</sub> and O<sub>ads</sub>) were estimated by measuring the ratio between the areas of the O1s and Ru3d<sub>5/2</sub> peaks. The as-calculated value was then compared with the corresponding value for the oxygen saturation on the Ru(0001) surface. The saturated coverage was assumed to be equal to 0.5 ML [9].

## 3. Results

### 3.1. The adsorption of NO on the Ru(0001) surface

The studies of NO on the Ru(0001) surface [7–10, 12,14,18,21–24] mainly focused on the low-temperature adsorption when the well-ordered adsorption layers were formed. The diffusion ability of the species in such layers is supposed to be low and, therefore, the low-temperature systems cannot adequately represent the behaviour of the “real-world” ruthenium catalysts. In order to obtain some guidance for the conditions when the diffusion processes play an important role (see for instance [17]), we studied the adsorption of NO and O<sub>2</sub> on the Ru(0001) surface at room and elevated temperatures. The XPS results are summarised in Fig. 1.

The O<sub>ads</sub> layer after exposure of the Ru(0001) surface to 100 L O<sub>2</sub> at 340 K showed a narrow peak at 529.8 eV in the O1s region (Fig. 1(a)). The peak parameters such as the peak position, the intensity, the FWHM and the shape did not change as the adsorption temperature increased up to 400 K (spectra not shown here). Two well-resolved peaks in both the O1s and N1s regions (Fig. 1(b))

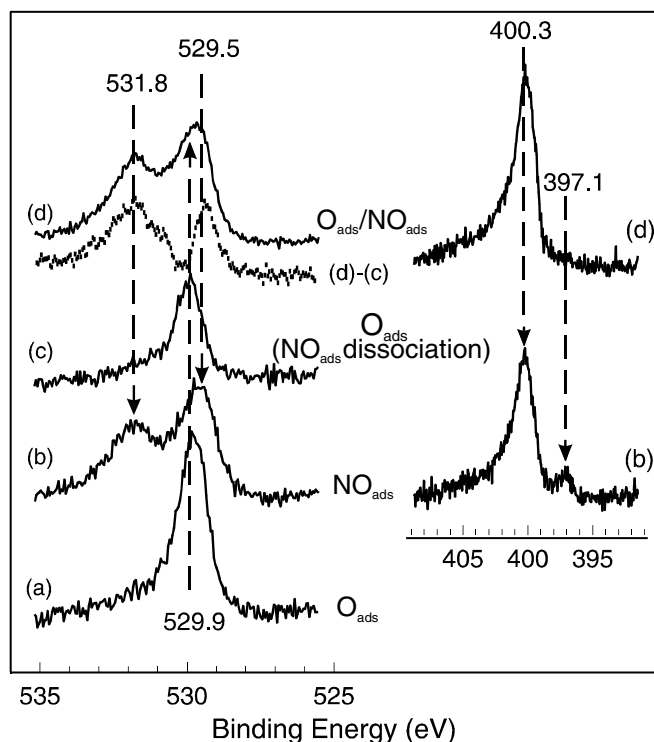


Fig. 1. O 1s and N 1s XPS spectra obtained from (a) the  $O_{ads}$  layer (100 L  $O_2$  at 340 K), (b) the saturated  $NO_{ads}$  layer (100 L NO at 300 K), (c) layer (b) heated in UHV at 700 K, (d) layer (c) exposed to 100 L NO at 300 K. The differential spectrum (d)–(c) is plotted as dots.

were obtained from the Ru(0001) surface exposed to NO up to saturation (100 L, 300 K). Peak assignments were performed based on the literature data summarised in Table 1. The two peaks at 400.3 and 397.1 eV in the N 1s core level spectra were assigned to molecularly adsorbed NO and  $N_{ads}$ , respectively [9,12]. We also observed the N 1s peak at 397.1 eV after saturating the Ru(0001) surface with  $N_{ads}$  by the decomposition of  $NH_3$ . The presence of the  $N_{ads}$  species proved that NO dissociates during adsorption. The two molecular states of  $NO_{ads}$ , threefold-

bridge and on-top, could not be resolved in the N 1s core level spectra and, therefore, these states were characterised by the broad peak at 400.3 eV [9]. According to the literature [7,9,17], NO adlayer was supposed to be composed of the two molecular states,  $v_1$  (threefold bridge) and  $v_2$  (on-top), and the dissociation products:  $O_{ads}$  and  $N_{ads}$ . Two O 1s peaks at 529.7 and 531.8 eV were associated with these molecular  $NO_{ads}$  and  $O_{ads}$  species formed during NO dissociation. As seen in Table 1, the threefold coordinated  $NO_{ads}$ ,  $v_1$ , and  $O_{ads}$  are characterised by the overlapping O 1s peaks. The presence of  $O_{ads}$  on the surface was indirectly supported by the N 1s peak at 397.1 eV assigned to  $N_{ads}$ . Since the  $N_{ads}$  species was found and since the  $O_{ads}$  species was supposed to be more stable than  $N_{ads}$  [3,8,9,29],  $O_{ads}$  should remain on the surface after NO dissociation.

In order to distinguish between the molecular and dissociative states of  $NO_{ads}$ , a saturated  $NO_{ads}$  layer was heated in UHV to 700 K. According to the literature [8,9,29], heating leads to  $NO_{ads}$  decomposition and desorption;  $N_{ads}$  recombines and desorbs as  $N_2$ ;  $O_{ads}$  remains on the surface. Indeed, as shown in Fig. 1(c), the XPS spectrum obtained after  $NO_{ads}$  layer heating showed a single peak at 529.9 eV, which was identical to those observed after  $O_2$  adsorption (Fig. 1(a)). The only difference was that the coverage after  $O_2$  adsorption was two times higher than the  $O_{ads}$  coverage after  $NO_{ads}$  decomposition.

Further exposure of  $O_{ads}/Ru(0001)$ , which was prepared through  $NO_{ads}$  thermal decomposition, to 100 L NO at 300 K restored the N 1s peak at 400.3 eV and the O 1s peaks at 529.5 ( $v_1$ ) and 531.8 eV ( $v_2$ ) as shown in Fig. 1(d). The absence of the N 1s peak at 397.1 eV showed that no dissociative adsorption of  $NO_{ads}$  occurred. So the  $O_{ads}$  species inhibited dissociation of nitric oxide but both the  $v_1$  and  $v_2$  molecular states of  $NO_{ads}$  were recovered. The total amount of  $NO_{ads}$  on the  $O_{ads}/Ru(0001)$  surface decreased by 25% in comparison to the Ru(0001) surface. The amount of on-top coordinated  $NO_{ads}$  remained approximately constant, while the amount of threefold  $NO_{ads}$  decreased twofold. So, the presence of  $O_{ads}$ , which is presumably in the threefold-hollow coordination, inhibited NO adsorption in the threefold hollow site. Indeed, the similar effect was observed by TPD, when NO was over an oxygen-covered Ru(0001) [25]. First, at 2.3 L predosed  $O_2$  the amount of  $NO_{ads}$  that dissociates was reduced to 30%. Second, in the presence of pre-adsorbed  $O_{ads}$ ,  $NO_{ads}$  desorbed in a single TPD peak corresponding to the  $v_2$  state of  $NO_{ads}$  on a clean surface [25].

The thermal stability of the saturated  $NO_{ads}$  layer was studied by stepwise heating in UHV. The saturated  $NO_{ads}$  layer was prepared by exposure of 10 L NO on the Ru(0001) surface at room temperature. After each heating, the sample was cooled and the O 1s and N 1s core level spectra were accumulated at room temperature as shown in Fig. 2. The spectra were curve-fitted assuming a Doniac–Sunijc peak shape [30]. The O 1s region was fitted with three peaks at 529.5, 529.9 and 531.7 eV, whereas the

Table 1  
BE of O 1s and N 1s peaks of surface species formed by NO adsorption on the Ru(0001) surface

Species	O 1s BE (eV)	N 1s BE (eV)	References
$v_1$ - $NO_{ads}$ the threefold position	530.3–530.7	399.6–399.9	[9,12,22,23]
$v_2$ - $NO_{ads}$ the on-top position	531.8	400.0–400.1	[9,12,22,23]
$O_{ads}$ (NO dissociation)	529.8–530.1	–	[9,12]
$N_{ads}$ (NO dissociation)	–	396.9–397.3	[9,12]
$v_1$ - $NO_{ads}$ the threefold position	529.4	400.4	This article
$v_2$ - $NO_{ads}$ the on-top position	531.8	400.4	This article
$O_{ads}$ (NO dissociation)	529.8–529.9	–	This article
$N_{ads}$ (NO dissociation)	–	397.1	This article

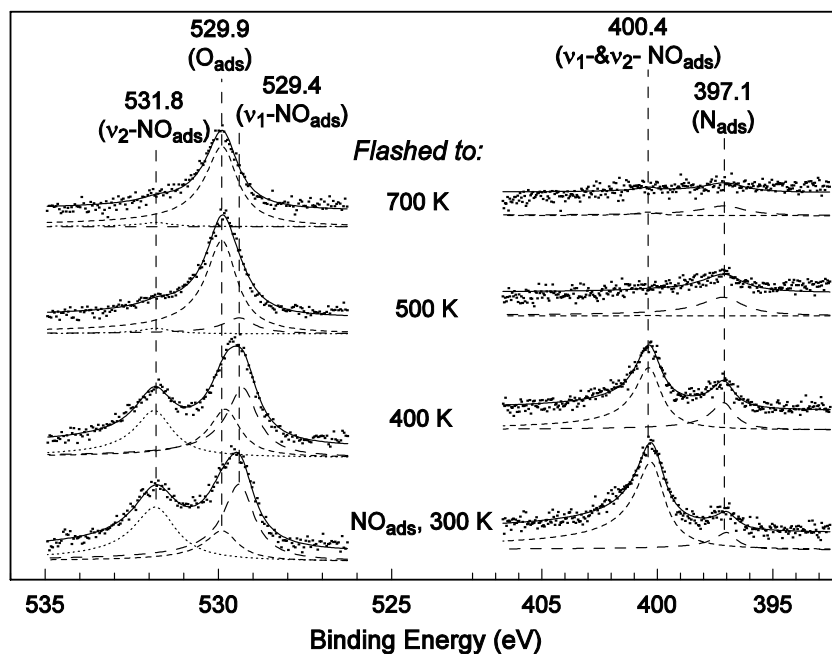


Fig. 2. Raw O 1s and N 1s XP spectra (dots) measured after saturating the Ru(0001) surface at 300 K with NO and after subsequent flashing to the given temperature in vacuum. The curve fit of the O 1s and N 1s lines was done assuming a Doniac–Sunijc peak shape.

N 1s core level spectra was described by two peaks at 397.1 and 400.4 eV (Fig. 2). The oxygen peaks were assigned based on the discussion above and the literature data [7,9,17]: the peaks at 529.5 and 531.7 eV were assigned to threefold,  $v_1$ , and on-top,  $v_2$ , coordinated  $\text{NO}_{\text{ads}}$  respectively; the peak at 529.9 eV was attributed to  $\text{O}_{\text{ads}}$ . The N 1s peaks at 397.1 and 400.4 eV were the features of  $\text{N}_{\text{ads}}$  and the molecular states of  $\text{NO}_{\text{ads}}$ , respectively. The coverage of the adsorbed species as a function of temperature is shown in Fig. 3. NO dissociation at RT led to an  $\text{O}_{\text{ads}}$  concentration that was slightly higher than the corresponding number for  $\text{N}_{\text{ads}}$ . Then, the coverage of NO dissociation products,  $\text{O}_{\text{ads}}$  and  $\text{N}_{\text{ads}}$ , increased with temperature. As shown in Fig. 3, the  $\text{N}_{\text{ads}}$  coverage passed through a maximum at 400 K and then dropped to zero. The coverage of  $\text{O}_{\text{ads}}$  demonstrated a steady growth up to 500 K and then remained unchanged. The growth of  $\text{O}_{\text{ads}}$  coverage correlated well with decreasing  $\text{NO}_{\text{ads}}$  coverage, reflecting dissociation and desorption of nitric oxide.  $\text{NO}_{\text{ads}}$  desorption/dissociation finished after heating at 500 K.

### 3.2. The reduction of NO with $\text{H}_2$ on the Ru(0001) surface

The reaction between NO and  $\text{H}_2$  was studied both on the originally clean Ru(0001) surface and the oxygen-covered surface at 320 and 390 K. These temperatures corresponded to the NO conversion of 50% and 100%, respectively [27]. Prior to each XPS measurement, Ru(0001) was treated for 10 min in a 30:1 mixture of  $\text{H}_2$  and NO (total pressure =  $10^{-4}$  mbar) in the preparation chamber. The reaction mixture was pumped out and then

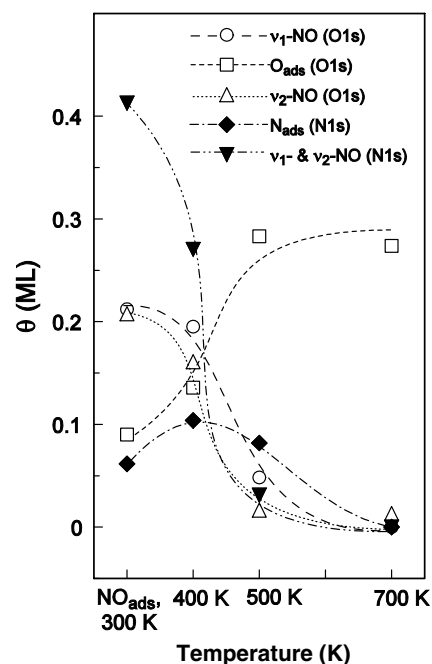


Fig. 3. The coverage of the adsorbed species as a function of the flashing temperature, the calculations were done basing on the results of the curve fit analysis.

the crystal was cooled to 320 K and transferred to the analysis chamber within 1 min.

Fig. 4 shows the O 1s and N 1s spectra measured after the steady-state reaction at 390 K on the originally clean Ru(0001) surface. The molecularly adsorbed NO in the linear on-top (531.7 eV) and threefold (529.4 eV) positions were found on the surface after the reaction. Since the



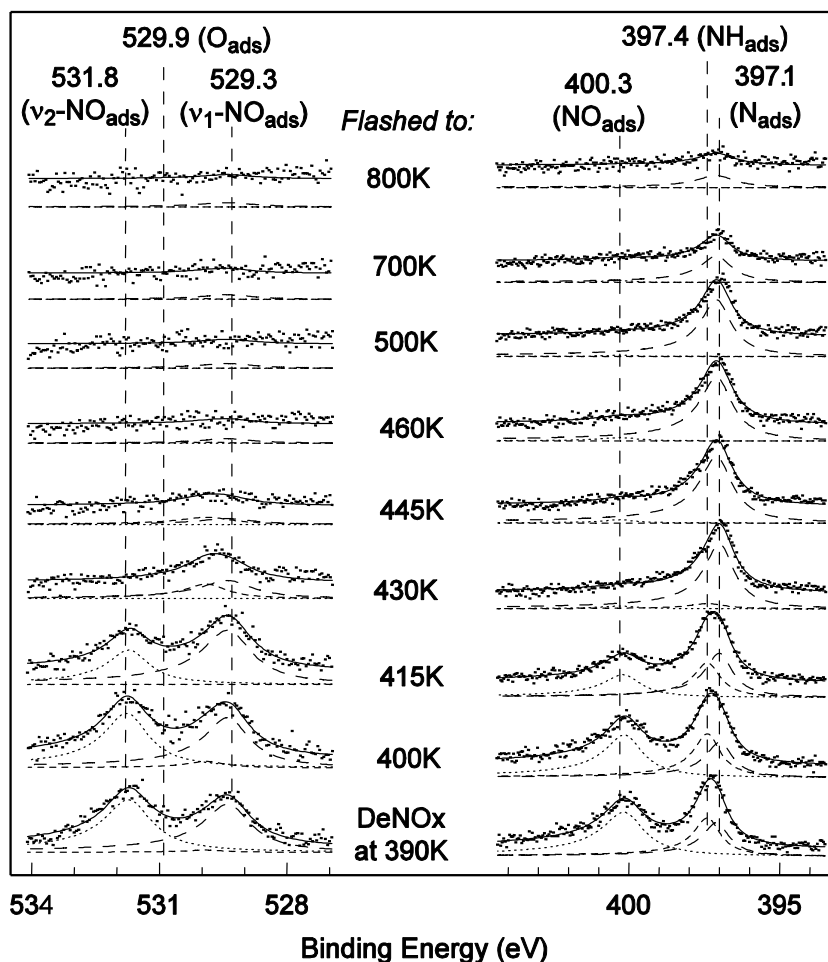


Fig. 4. Raw O 1s and N 1s XP spectra (dots) taken after exposure of the clean Ru(0001) surface to a 30:1 mixture of  $H_2$  and NO (total pressure =  $10^{-4}$  mbar) at 390 K for 10 min and after heating the as-prepared adlayer stepwise under vacuum. The curve fit of the O 1s and N 1s lines was done assuming a Doniac–Sunjic peak shape.

FWHM of the peaks was approximately 1 eV, the existence of the peak at 529.9 eV due to  $O_{ads}$  could be unambiguously ruled out. One can conclude that no  $O_{ads}$  was on the surface after the reaction. Two peaks at 400.4 and 397.4 eV were observed in the N 1s core level spectra. The peaks at 400.4 eV could be unambiguously assigned to  $NO_{ads}$ . The peak at 397.4 eV was slightly shifted towards higher BE in comparison to the  $N_{ads}$  peak at 397.1 eV. Also, the peak at 397.4 eV was found to be broader than the  $N_{ads}$  peak, therefore, this peak was tentatively assigned to a N-containing species other than  $NO_{ads}$  and  $N_{ads}$ .

We observed the peak at 397.4 eV during  $NH_3$  decomposition on the Ru(0001) surface and assigned it to adsorbed NH fragments. This assignment was in agreement with all the available literature data summarised in Table 2. Unfortunately, not much XPS data on  $NH_x$  fragments with clear assignment of the peak positions were available in the literature (Table 2). Sun et al. [31] and Weststrate et al. [32] reported the BE of 397.5 eV and 397.6 eV for the  $NH_{ads}$  species on the Pt(111) and Ir(110) surfaces, respectively. Assuming the correctness of the above out-

Table 2

Core level BE values of N-containing species adsorbed on different surfaces

Sample	BE (eV)				Reference
	$NH_{3,ads}$	$NH_{2,ads}$	$NH_{ads}$	$N_{ads}$	
Fe(poly)	400.0				[37]
Fe(110), (111)	400.0		397.3	396.6–397.0	[38]
Al(poly)	400.0	399.4	398.0	397.0	[39]
Amorphous Si	400.1	398.6	398.0	397.4	[40]
GaAs(110)	400.1	398.5			[41]
Pt(111)	399.3	397.5	397.5		[31]
Ir(110)	399.5–400.1		397.6	396.5	[32,42]
Ru(0001), (1110)	400.0	398.1	397.5–397.6	397.1–397.3	[12]
Ru(0001)			397.4	397.1	This work

lined BE assignments, we suggested that the  $NH_{ads}$  species was present on the Ru(0001) surface during the steady-state catalytic reduction of nitric oxide with excess hydrogen. The other adsorbed species were molecularly on-top and bridge coordinated  $NO_{ads}$  and probably  $N_{ads}$ .

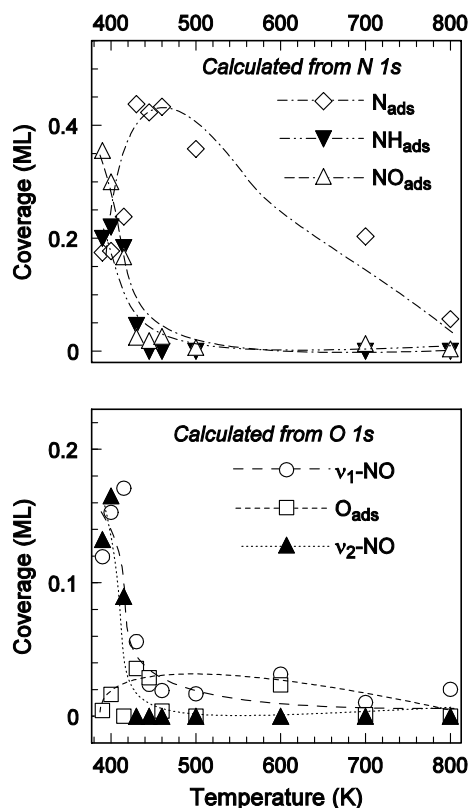


Fig. 5. The coverage of the adsorbates on the treated surface as a function of flashing temperature (see treatment conditions in the caption of Fig. 4). The calculations were done basing on the results of the curve fit analysis.

In order to identify the surface species, the Ru(0001) surface was heated after treatment in the reaction mixture at 390 K for 10 min in vacuum. The XPS spectra were collected at room temperature as shown in Fig. 4. The coverage of the adsorbed species as a function of temperature is shown in Fig. 5. The adlayer did not change up to 415 K. But after heating at 430 K, dramatic changes were observed. First, the O 1s peak at 531.7 eV, which is a characteristic of the on-top coordinated  $\text{NO}_{\text{ads}}$  species,  $v_2$ , disappeared. Second, the peak at 529.5 eV, which was assigned to the threefold coordinated  $\text{NO}_{\text{ads}}$  species,  $v_1$ , shifted to 529.7 eV. This reflected the appearance of  $\text{O}_{\text{ads}}$ . Simultaneously, the N 1s peak at 400.4 eV, which is a fingerprint of molecularly adsorbed states of NO,  $v_1$  and  $v_2$ , also disappeared. This pointed to dissociation and/or desorption of  $\text{NO}_{\text{ads}}$ . The threefold coordinated  $\text{NO}_{\text{ads}}$  species showed a slightly higher thermal stability in comparison to the linearly coordinated form (Fig. 5). Therefore, the threefold coordinated  $\text{NO}_{\text{ads}}$  species was supposed to be an intermediate for NO dissociation: due to dissociation, the threefold  $\text{NO}_{\text{ads}}$  might get depleted but the linear form converts into the threefold  $\text{NO}_{\text{ads}}$ . The appearance of  $\text{O}_{\text{ads}}$  coincided with the low-BE shift of the N 1s peak from 397.4 eV to 397.1 eV. This shift cannot be explained by a technique artefact because no deviation was observed for the other peaks in particular for the  $\text{Ru}3d_{5/2}$  peak. Also, the low-BE shift of the N 1s peak was consistent during

numerous heating experiments. Therefore, the low-BE shift could be assigned to the transformation of  $\text{NH}_{\text{ads}}$  into the  $\text{N}_{\text{ads}}$  species.

All oxygen-containing species disappeared after heating at 445 K. On the other hand, the adsorbed nitrogen was detected even after heating to 800 K. It is remarkable that in the presence of co-adsorbed atomic oxygen, the full desorption of all nitrogen-containing species was achieved by heating below 700 K (compare with Fig. 2). The conclusion could be drawn that  $\text{O}_{\text{ads}}$  essentially destabilises the co-adsorbed  $\text{N}_{\text{ads}}$ . This conclusion is a good agreement with the TPD data reported in Ref. [25]. There it was found that  $\text{N}_2$  forms between 600 K and 800 K when a  $\text{NO}_{\text{ads}}$  layer was heated in the presence of  $\text{H}_2$ , whereas heating of a  $\text{NO}_{\text{ads}}$  layer in vacuum led to  $\text{N}_2$  desorption between 400 K and 600 K. This finding corroborates the hypothesis about the repulsive interaction effect of  $\text{O}_{\text{ads}}$  on  $\text{N}_{\text{ads}}$ .

The O-containing species disappeared already at temperatures as low as 445 K and this could not be due to oxygen desorption. As shown in Fig. 2, oxygen remained on the surface after heating to 700 K. Heating above 1100 K is required to remove oxygen.  $\text{O}_{\text{ads}}$  was supposed to be consumed in the course of the reaction with hydrogen-containing species. As shown in Fig. 4, the O-containing species disappear simultaneously with the consumption of the  $\text{NH}_{\text{ads}}$  species and the formation of  $\text{N}_{\text{ads}}$ . This fact unambiguously pointed to the reaction between  $\text{O}_{\text{ads}}$  and  $\text{NH}_{\text{ads}}$ . Water formed during this reaction should desorb immediately because the temperature was too high for the  $\text{H}_2\text{O}$  and OH adsorption. This was consistent with the fact that no new peaks appeared in the O 1s region by XPS or in the valence zone by UPS.

The Ru(0001) surface was examined after steady-state  $\text{NO} + \text{H}_2$  reaction at 320 K. Fig. 6 shows the O 1s and N 1s core level spectra obtained from the Ru(0001) surface after the reaction for 10 min at 320 and 390 K. The overall surface coverage was higher at the low reaction temperature. The change of the reaction temperature altered the relative concentration of the N-containing adsorbed species. At 320 K, where the conversion of NO was 50% for a Ru/MgO catalyst [27], the most abundant surface species was molecularly adsorbed NO (mainly in the threefold coordinated form) and the concentration of  $\text{N}_{\text{ads}}$  was low. At 390 K, where the conversion of NO was 100% for a Ru/MgO catalyst [27], the coverage of  $\text{N}_{\text{ads}}$  increased to a value comparable to the coverage of the  $\text{NH}_{\text{ads}}$  species, whereas  $\theta_{\text{NO}}$  reduced by almost 30%.

Finally, in order to clarify the effect of adsorbed oxygen, the reaction was also studied under the same experimental conditions at 390 K. The oxygen-covered surface was prepared by dosing 10 L NO at room temperature and flashing to 700 K to remove all N-containing species as discussed in Section 3.1. The initial presence of adsorbed oxygen on the surface did not seem to affect the reaction. The composition of the adlayer after the reaction both on the initially adsorbate-free and on the oxygen-covered surfaces was qualitatively and quantitatively the same (spectra not shown here).

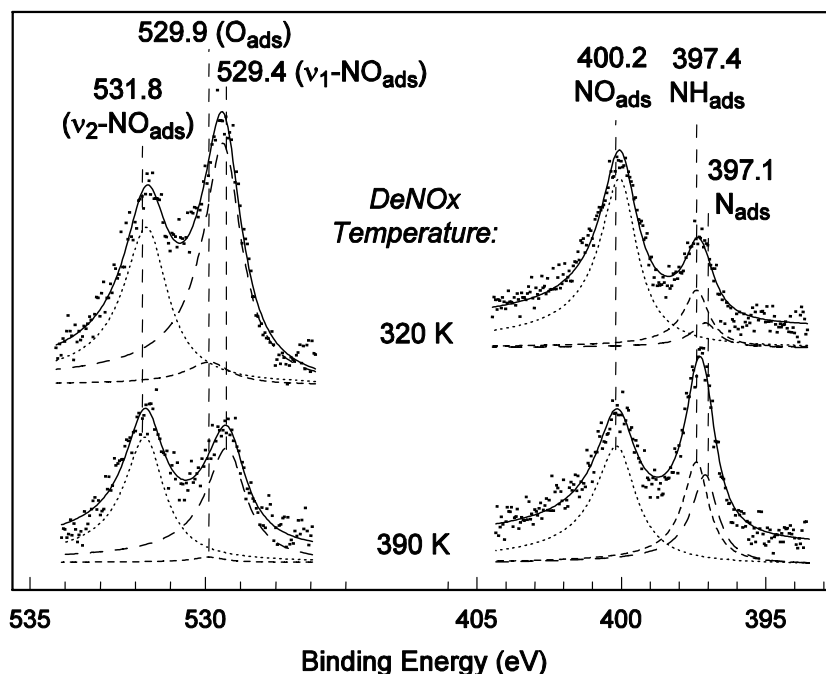


Fig. 6. O 1s and N 1s XP spectra taken after exposure of the clean Ru(0001) surface to a 30:1 mixture of H<sub>2</sub> and NO (total pressure = 10<sup>-4</sup> mbar) at 320 K and 390 K for 10 min.

## 4. Discussion

### 4.1. NO adsorption

As seen in Fig. 1, 0.25 ML pre-adsorbed oxygen is sufficient to block NO<sub>ads</sub> dissociation at RT completely. On the Ru(0001) surface at 300 K, NO dissociates predominantly at atomic steps to which the NO<sub>ads</sub> species migrate and from where the generated N<sub>ads</sub> and O<sub>ads</sub> atoms diffuse away [17]. However, O<sub>ads</sub> atoms may remain attached with the step sites and, thus, may cause inhibition of the “active sites”. The XPS results demonstrate that O<sub>ads</sub> coverage after NO adsorption was slightly higher than the corresponding value for N<sub>ads</sub>. The N<sub>ads</sub> species formed during NO dissociation was supposed to recombine and desorb as N<sub>2</sub>. This is in a good agreement with the data obtained from the Ru/MgO catalysis [3,27]. Thus, the partial recombination of N<sub>ads</sub> followed by N<sub>2</sub> desorption was found during an exposure of the Ru/MgO catalysis to NO at room temperature by applying frontal chromatography [3]. However, the comparison between a Ru(0001) single crystal and a Ru/MgO catalysis can be only qualitative because the density of defect sites on the well-ordered surface of a Ru(0001) single crystal is much lower than the corresponding value for the 200 Å supported Ru particles [3].

Our experiments demonstrated the destabilisation effect of the O<sub>ads</sub> species on N<sub>ads</sub>. On the O-free surface, N<sub>ads</sub> was observed after heating at 800 K (Figs. 4 and 5), whereas only a little of N<sub>ads</sub> was found on the O-containing surface after heating at 500 K (Figs. 2 and 3). Nagl et al. [20] reported that there is a phase equilibrium in the mixed N<sub>ads</sub> and O<sub>ads</sub> layer between the two-component 2 × 2 patches

and its dilute gas phase, i.e., an O-rich dense phase and N-rich lattice gas. Due to relatively weak N–O interaction in the dense phase, the enthalpy of the mixing is positive, therefore, the growth of 2 × 2 dense phase causes two-dimensional “vapour pressure” increases and N atoms might start to recombine and leave the surface.

According to HREELS data [7,8], at 150 K at low coverage, NO<sub>ads</sub> adsorbs only in the threefold coordinated adsorption states on the steps, v<sub>0</sub>, and on the terraces, v<sub>1</sub>. These states dissociated completely upon heating in UHV at 250–310 K. Since no new state formed upon heating, the threefold coordinated states were supposed to be an intermediate species for NO dissociation. Thomas and Weinberg [7] reported that at high coverage the threefold NO<sub>ads</sub> decomposed first and only then the linearly coordinated species dissociated. The hypothesis about the threefold coordinated NO<sub>ads</sub> as an intermediate for dissociation agrees with a quantum-mechanic modelling predicting a higher value of the π back donation to the anti-bonding molecular orbital of NO<sub>ads</sub> for the threefold coordinated species [21]. It is remarkable that an N–O bond length of the linearly coordinated NO<sub>ads</sub>, v<sub>2</sub>, was calculated to be equal 1.20 ± 0.01 Å and 1.13 ± 0.06 Å from NEXAFS spectra [14] and from LEED-IV data [19,22] respectively, whereas N–O bond in the threefold coordination, v<sub>1</sub>, was elongated to 1.32 ± 0.02/1.28 ± 0.02 Å (NEXAFS) [14] and 1.24 ± 0.07/1.22 ± 0.06 Å (LEED-IV) [19,22]. The N–O bond in the threefold state elongates in comparison to in the linearly coordinated form due to a substantially stronger π back donation [21]. The π back donation should result in weakening the N–O bond. Therefore, this also points to the higher ability of NO to dissoci-



ate in the threefold state. The indirect experimental proof observed by us is that the presence of  $O_{ads}$ , which is presumably in the threefold-hollow coordination, inhibited NO adsorption in the threefold hollow coordination and no dissociation of  $NO_{ads}$  was found (Fig. 1).

In our heating experiments, the threefold and linearly coordinated  $NO_{ads}$  species decomposed almost simultaneously. However, this does not contradict the hypothesis about the threefold coordinated  $NO_{ads}$  as an intermediate for NO dissociation. This fact underlines the importance of the surface diffusion. At room temperature the diffusion is fast enough (i) to clean the “active sites” from the product of dissociation and (ii) to bring a new portion of a reagent. This is not the case at low temperatures where the dissociation products remain where they formed and the adsorption layer could not be mixed by diffusion.

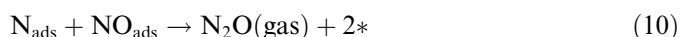
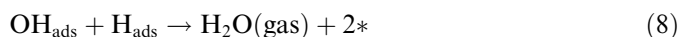
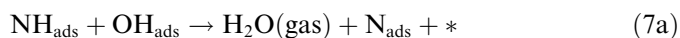
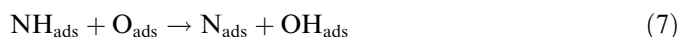
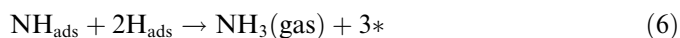
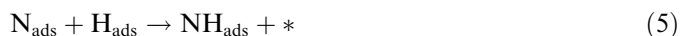
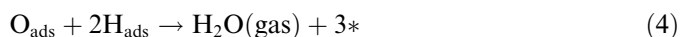
#### 4.2. $NO + H_2$ reaction

The catalytic reduction of NO with  $H_2$  on ruthenium is a process with an extremely high selectivity to  $N_2$ , whereby less than 1% of the fed NO is converted into  $NH_3$  at 100% conversion (see Ref. [3] and references therein). On the other hand, ruthenium is a highly active catalyst for the synthesis of ammonia from nitrogen and hydrogen (see Ref. [33] and references therein). Moreover, it has been proven that the first hydrogenation step of  $N_{ads}$  to  $NH_{ads}$  is the rate-determining step of ammonisation in co-adsorbed  $N_{ads}/H_{ads}$  layers [34]. Is the formation of the  $NH_{ads}$  species observed in the present in contradiction with the already mentioned high selectivity to  $N_2$  in the selective catalytic reduction of NO?

One of the main questions on this issue is the reliability of the assignment of the  $NH_{ads}$  species. The XPS data unambiguously demonstrated (Fig. 4) that the Ru(0001) surface after exposure to a reaction mixture at 390 K did not contain  $O_{ads}$ . Moreover, the heating of this surface did not lead to  $O_{ads}$  formation and the curve fitting gave no indication of any 529.9 eV peak.  $O_{ads}$  does not desorb from the Ru(0001) surface at discussed temperature. The only reasonable explanation for the “missing” of  $O_{ads}$  could be the reaction to form water. So, some source of hydrogen must exist on the surface after the reaction.  $H_{ads}$  can be ruled out because according to the literature [35], hydrogen does not adsorb at 300 K on the surface covered by  $N_{ads}$ . Therefore, the only possible source of hydrogen could be  $NH_x$  species. According to the literature data in Table 2, the N1s peak from  $NH_{3,ads}$  and  $NH_{2,ads}$  are expected between 397.5 eV and 400 eV. In our experiments, the peak at 397.4 eV was observed. The rule of thumb is that the  $\Delta BE$  between different  $NH_{x,ads}$  species is approximately 1 eV (see for instance Refs. [31,32] and Table 2). From this point of view, the  $\Delta BE$  between  $NH_{ads}$  (397.4 eV) and  $N_{ads}$  (397.1 eV), which is only 0.3 eV, does not look very convincing. On the other hand, the higher BE shift of the N1s and decrease of its FWHM were repetitiously observed during all heating of the surface after

the reaction. The analysis was hindered by the presence of the  $N_{ads}$  species resulting in the peak at 397.1 eV. However, the curve-fitting performed with the several experimental sets applying the same fitting parameters unambiguously pointed to the two components at 397.4 eV and 397.1 eV. Also, since the peak splitting is small, the peak at 397.4 eV obviously cannot be assigned to  $NH_{2,ads}$  species. The vast nature of the experimental data along with the literature allowed us safely to assume the presence of the  $NH_{ads}$  species on the surface after the reaction.

The other question concerns the role of the  $NH_{ads}$  species in the reaction mechanism. The following simple reaction mechanism can be suggested.



Here \* denotes a vacant site on the surface. We do not distinguish the types of active sites, which can vary for the different reaction steps. However, even this primitive mechanism is able to explain peculiarities of  $NO + H_2$  reaction. The  $NH_{ads}$  species can be an intermediate for ammonia (step (6)).  $NH_{ads}$  oxidation by OH group was also included (7a). The similar reaction step was proposed by van den Broek et al. [36] in the case of ammonia oxidation on platinum and iridium. The hydrogenation of  $NH_{ads}$  to  $NH_3$  can be kinetically limited due to low  $H_{ads}$  coverage in the presence of  $N_{ads}$  as discussed above (see Ref. [35]).  $NH_{2,ads}$  which could be formed from the  $NH_{ads}$  species, likely is not stable and cannot be detected. The curve-fitting analysis of the XPS spectra after reaction did not show a component between 398 eV and 399 eV. So,  $NH_{ads}$  could be involved in  $N_2$  formation through steps (7) and (7a).

The indirect proof of the kinetic limitation of  $NH_{ads}$  in the hydrogenation to  $NH_3$  was found during the microkinetic investigation of NO reduction on MgO-supported ruthenium catalysts [3]. It was observed that the high selectivity to  $N_2$  strongly depends on the catalyst surface coverage in the following way: at high coverage, the presence of adsorbed NO and of its dissociation products shifts the dissociative adsorption equilibrium of  $H_2$ , thus hindering the full hydrogenation of adsorbed nitrogen to ammonia; as soon as the surface coverage lowers and sufficient  $H_{ads}$  species are available, the main product will be  $NH_3$ . This is

consistent with the conclusions made above. According to the XPS results, after the reaction the surface was covered with  $\text{NO}_{\text{ads}}$ ,  $\text{N}_{\text{ads}}$  and  $\text{NH}_{\text{ads}}$ . Therefore hydrogen coverage should be low and  $\text{NH}_{\text{ads}}$  hydrogenation to  $\text{NH}_3$  should be hindered (step (6)).

The XPS data (Fig. 6) showed that  $\text{NO}_{\text{ads}}$  coverage after the reaction at 320 K was higher than the corresponding values after the reaction at 390 K but the amount of  $\text{N}_{\text{ads}}$  and  $\text{NH}_{\text{ads}}$  was less than at 390 K. Also the threefold  $\text{NO}_{\text{ads}}$  was the dominating species at 320 K. On the Ru/MgO catalyst [27], the temperatures of 320 K and 390 K corresponded to 50% and 100% NO conversions, respectively. These two facts are reasonably consistent. So, high NO coverage might cause decreased NO conversion through inhibition of  $\text{NO}_{\text{ads}}$  dissociation due to the absent of vacant sites (step (3)). This might indicate that  $\text{NO}_{\text{ads}}$  dissociation might be the rate-determining step.

De Wolf et al. [25] reported about poisoning the Ru surface by  $\text{O}_{\text{ads}}$  during  $\text{NO} + \text{H}_{\text{ads}}$  reaction. This effect was not detected in the present study. The surface composition after the reaction on the surface deliberately covered with  $\text{O}_{\text{ads}}$  was identically those after the reaction on the originally clean surface. The XPS technique also did not find  $\text{O}_{\text{ads}}$  species. The disagreement with Ref. [25] could be explained by different reaction conditions used in our experiments.

## 5. Conclusions

The investigation of the adsorption of NO at room temperature showed, in agreement with the literature, that NO partially dissociated on the Ru(0001) surface already at room temperature, whereas the major fraction was molecularly adsorbed. Two different states (on-top and threefold coordinated) of adsorbed NO could be distinguished. Dissociation of  $\text{NO}_{\text{ads}}$  was suggested to occur through the formation of the threefold coordinated NO species. The strong destabilisation of adsorbed nitrogen by the presence of co-adsorbed oxygen was observed.

After steady-state NO reduction, the adsorption layer consisted of molecular NO both linearly and bridge coordinated,  $\text{NH}_{\text{ads}}$  and  $\text{N}_{\text{ads}}$  species, which relative concentrations depended on the reaction temperature. The coverage of the  $\text{NH}_{\text{ads}}$  and  $\text{N}_{\text{ads}}$  species was higher after the reaction at 390 K than the corresponding values for the reaction at 320 K. NO dissociation was supposed to be a rate-determining step. The  $\text{NH}_{\text{ads}}$  species might be involved in the mechanism of  $\text{N}_2$  formation.

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